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Original Research article

Acidic Ionic Liquid Based Silica-Coated Fe_3O_4 Nanoparticles as a New Nanomagnetic Catalyst for Preparation of Aryl and Heteroaryl Thiocyanates

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ABSTRACT

In this research study, acidic ionic liquid based silica-coated Fe_3O_4 nanoparticles $[Fe_3O_4@SiO_2@(CH_2)_3\text{-}Py]HSO_4$ as an efficient and reusable magnetic nanocatalyst was synthesized and characterized using the FT-IR, TEM, VSM, XRD, and TGA analysis. The catalytic performance of the $[Fe_3O_4@SiO_2@(CH_2)_3\text{-}Py]HSO_4$ was evaluated towards the regioselective thiocyanation of aromatic and heteroaromatic compounds with KSCN as a thiocyanate source afforded the corresponding aryl and heteroaryl thiocyanates derivatives **2a-n** at room temperature in H_2O_2 as a clean oxidant and ethanol as a green solvent. A broad range of products **2a-n** was synthesized high yields (up to yield 97%) under the mild reaction conditions.

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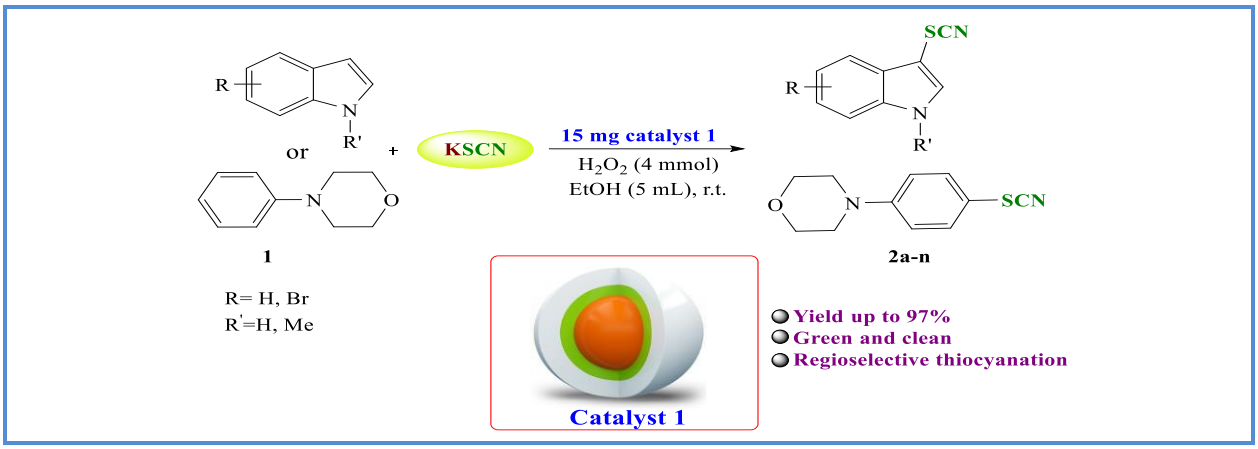
Graphical Abstract



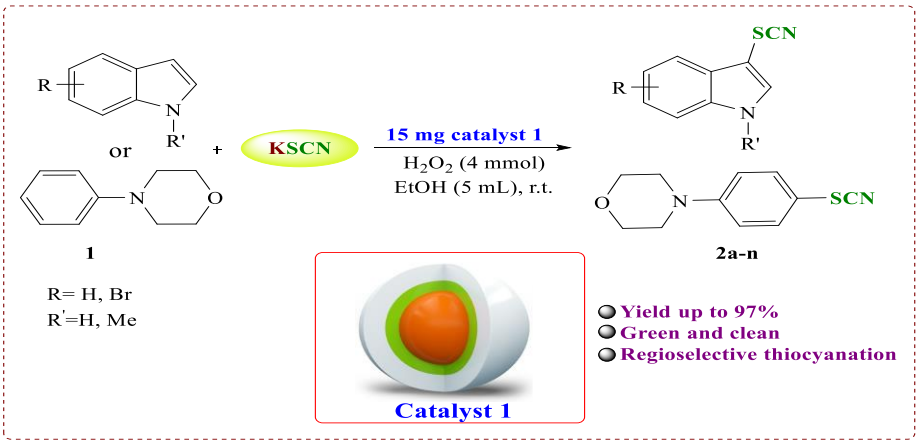
Introduction

As energy has been a vital concern, the use of catalysis especially magnetic nanocatalysts as a new sustainable method has attracted a great deal of attention [1]. Magnetic nanocatalysts have stability and competence rather than traditional catalysts, and they showed a great potential in the domain of research. MNPs have received praiseworthy attention as catalyst, as they have various advantages including, simple and convenient recovery and recyclability, easy preparation, large surface area, low-priced, and low toxicity [2-4]. MNPs have widely used as efficient and suitable catalysts for various organic transformations such as Knoevenagel, C–C coupling reactions, oxidation of sulfides, benzyl halides, suzuki coupling reactions, oxidative coupling of thiols, esterification reaction, and epoxidation of alkenes [5, 6]. Also, MNPs have attracted a great attention due to their applications in magnetic resonance imaging [7], magnetic fluids [8], biology, medical [9], environmental remediation [10], and data storage industries [11].

The electrophilic thiocyanation of aromatic and heteroaromatic compounds with the partner of potassium thiocyanate (KSCN) represents an essential direct method for the synthesis of the aryl and heteroaryl thiocyanates derivatives [12]. Aryl and heteroaryl thiocyanates are fascinating species as their compounds are the useful intermediates for formation of the carbon-sulfur bond [13, 14]. As an atom-economic thiocyanate (SCN) source in synthetic chemistry, potassium thiocyanate (KSCN) is adequate and the simplest molecule due to its high availability. Therefore, the direct thiocyanation of aromatic and heteroaromatic compounds is of importance. Many reported the electrophilic thiocyanation of the catalysts such as iodine [15], IL-$OPPh_2$ [16], I_2O_5 [17], CAN [18], Selectfluor™ [19], HCl [20], diethyl azodicarboxylate [21], $Mn(OAc)_3.2H_2O$ [22], *N*-thiocyanatosuccinimide [23], pentavalent iodine [24], [Msei] SCN [25], IBX [26], (PSMIM) SCN [27],

SSA and SBSA [28], potassium peroxydisulfate/copper (II) sulfate [29], Visible-light [30], {SiO_2@[Pyridine-SO_3H]SCN and {[PSA]Cl} [31], Phthalic acid [32], and Fe_3O_4-IL-HSO_4 [33]. However, some of the aforementioned methods suffer from unrecoverable, toxicity, high cost, low yields, harsh reaction conditions, long reaction time, and tedious workup. Therefore, an efficient, simple and environmentally benign transformation of aromatic and heteroaromatic compounds (pyrrole, anilines, and indoles) into aryl and heteroaryl thiocyanates is highly desired.

Previous works have depicted the acidic ionic liquid based silica-coated Fe_3O_4 nanoparticles as an efficient and reusable magnetic nanocatalyst for synthesis of polyhydroquinoline derivatives [34]. Therefore, many studies have been conducted on magnetic nanocatalysts and their applications, and in this study developed acidic ionic liquid-based silica-coated Fe_3O_4 nanoparticles, followed by assessing the its catalytic capacity in aromatic and heteroaromatic compounds (pyrrole, anilines, and indoles) to their corresponding aryl and heteroaryl thiocyanates **2a-n** derivatives (Scheme 1).



Scheme 1. Synthesis of aryl and heteroaryl thiocyanates derivatives using [Fe_3O_4@SiO_2@$(CH_2)_3$-Py]HSO_4 as catalyst

Experimental

General procedure for the synthesis of [Fe_3O_4@SiO_2@$(CH_2)_3$-Py]HSO_4

The acidic ionic liquid based silica-coated Fe_3O_4 nanoparticles [Fe_3O_4@SiO_2@$(CH_2)_3$-Py]HSO_4 was prepared according to the method presented in [34], and confirmed by conducting various analysis techniques including, the Fourier-transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), value stream mapping (VSM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) [34].

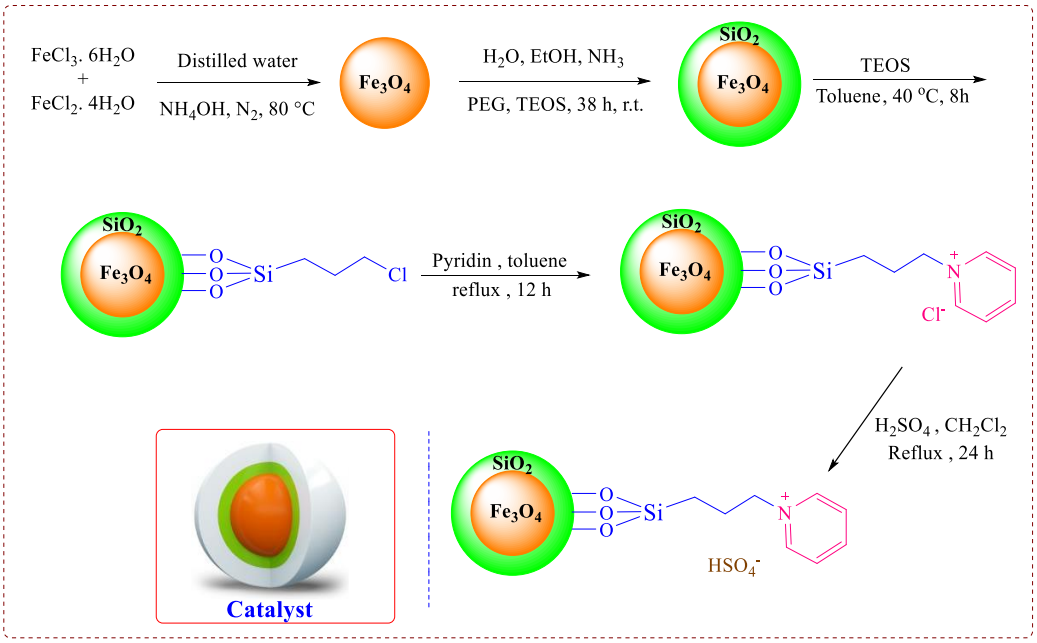
General procedure for the synthesis of aryl and heteroaryl thiocyanates derivatives

15 mg of the nanomagnetic catalyst was added to a mixture of indole (1 mmol), KSCN (3 mmol), EtOH (5 mL) in a round-bottomed flask. Then, 4 mmol of H_2O_2 (30%) was added dropwise in 2-5

min. The obtained mixture was stirred at room temperature for proper time as indicated in Table 4. Reaction progress was monitored by TLC using a mixture of EtOAc and *n*-hexane as eluent (1:9). After completion of the reaction, to separate the magnetic nanocatalyst, $CHCl_3$ (2×10 mL) was added to the reaction mixture. After separating the catalyst by an external magnet, the pure product was obtained after extracted with $CHCl_3$ in good to high yield as indicated in Table 4.

Results and discussion

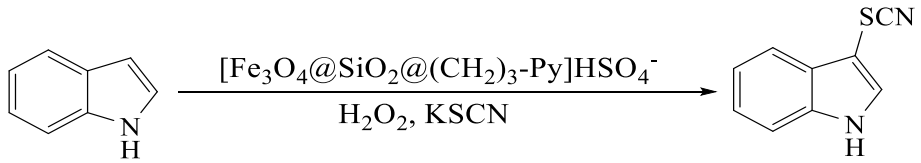
In continuation of our studies on the application of MNPs in organic reactions [35-37], our research group introduced the acidic ionic liquid based silica-coated Fe_3O_4 nanoparticles ($[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$) in 2019 for the synthesis of polyhydroquinoline derivatives [34]. The magnetic nanocatalyst was prepared easily in multi-step from the reaction between tetraethylorthosilicate (TEOS) with Fe_3O_4 nanoparticles afforded the corresponding $Fe_3O_4@SiO_2$. Then, treatment of the $Fe_3O_4@SiO_2$ by 3-chloropropyl) trimethoxysilane under the N_2 produced the $Fe_3O_4@SiO_2@(CH_2)_3\text{-Cl}$. In the next step, treatment of the $Fe_3O_4@SiO_2@(CH_2)_3\text{-Cl}$ by pyridine under the reflux conditions afforded the corresponding $[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]Cl$ and finally reacted with H_2SO_4 under the reflux conditions to produce the $[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4^-$ as a reusable magnetic nanocatalysts. Then, the catalyst was investigated using various techniques including, FT-IR, TEM, VSM, XRD, and TGA [34] (Scheme 2).



Scheme 2. Synthetic pathway for construction of new magnetic nanoparticles

Initially a model reaction was carried out upon the reaction of 1*H*-indole (1 mmol), KSCN (3 mmol), H_2O_2 (4 mmol) in the several of catalysts under the solvent-free conditions at room temperature to find out the best reaction promoter to the 3-thiocyanato-1*H*-indole **2a** (Table 1). The results revealed that the best data obtained at the presence of the $[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$ as a reusable magnetic nanocatalysts in with 93% yield after 10 min (Table 1, entry 4). As seen in the Table 1. (entries 1-4), the catalytic activity has increased both the yield and reaction time. It is related to the modification of the surface of Fe_3O_4 by basic and acidic species. Although the trityl chloride and trityl bromide as catalyst were low effective in the tested condition (25% and trace, Table 1, entries 6-7), $FeCl_3$ provided a lower yield after 30 min (33%, Table 1, entry 5). Then, the reaction was investigated in the different amount of catalyst (Table 1, entries 9–15).

Table 1. Optimization of catalyst for the synthesis of 3-thiocyanato-1*H*-indole **2a**

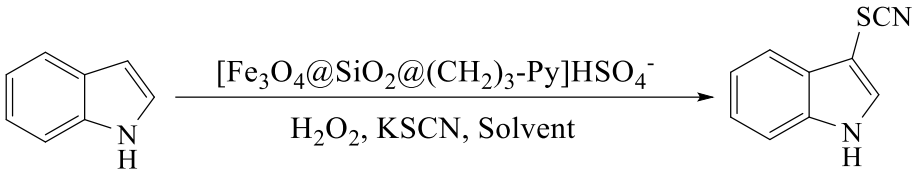


Entry	Catalyst (mg)	Load of catalyst	Time (min)	Yield (%)[a]
1	Fe_3O_4	15 mg	30	48
2	$Fe_3O_4@SiO_2$	15 mg	30	48
3	$Fe_3O_4@SiO_2@(CH_2)_3\text{-Cl}$	15 mg	30	60
4	$[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$	15 mg	10	93
5	$FeCl_3$	15 mol%	30	33
6	Trityl chloride	15 mol%	60	Trace
7	Trityl bromide	15 mol%	60	25
8	Catalyst-free	-	24 h	Trace
9	$[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$	1 mg	50	77
10	$[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$	3 mg	40	79
11	$[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$	5 mg	33	83
12	$[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$	10 mg	25	88
13	$[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$	20 mg	10	92
14	$[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$	25 mg	10	92
15	$[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$	30 mg	12	90

[a] Isolated yield

In the next study, a model reaction was carried out upon the reaction of 1*H*-indole (1 mmol), KSCN (3 mmol), H_2O_2 (4 mmol) in the various of solvents at ambient temperature to find the best reaction promoter to the 3-thiocyanato-1*H*-indole **2a** (Table 2). The results demonstrated that the best data obtained in EtOH at the presence of 15 mg of the $[Fe_3O_4@SiO_2@(CH_2)_3\text{-Py}]HSO_4$ as a reusable magnetic nanocatalysts with 97% yield after 10 min (Table 2, entry 1).

Table 2. Optimization of reaction conditions for synthesis of 3-thiocyanato-1*H*-indole

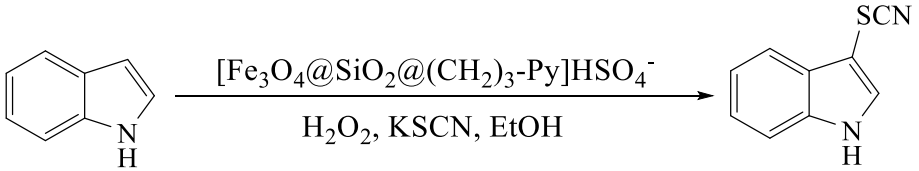


Entry	Solvent (mL)	Load of catalyst	Time (min)	Yield (%)[a]
1	EtOH	15 mg	10	97
2	H_2O	15 mg	10	95
3	EtOH: H_2O	15 mg	12	94
4	$CHCl_3$	15 mg	120	88
5	CH_2Cl_2	15 mg	110	87
6	EtOAc	15 mg	160	75
7	*n*-Hexane	15 mg	120	85
8	CH_3CN	15 mg	160	73
9	CH_3OH	15 mg	130	81

[a] Isolated yield

In addition, a model reaction was carried out upon the reaction of 1*H*-indole (1 mmol), KSCN (3 mmol), EtOH (5 mL) using various amount of H_2O_2 at room temperature to find the best reaction promoter to the 3-thiocyanato-1*H*-indole **2a** (Table 3). The results revealed that the best data obtained in EtOH (5 mL), H_2O_2 (4 mmol), $[Fe_3O_4@SiO_2@(CH_2)_3\text{-}Py]HSO_4$ (15 mg) as a reusable magnetic nanocatalysts with the yield of 97% after 10 min (Table 3, entry 2).

Table 3. Optimization of amount of H_2O_2 for synthesis of 3-thiocyanato-1*H*-indole



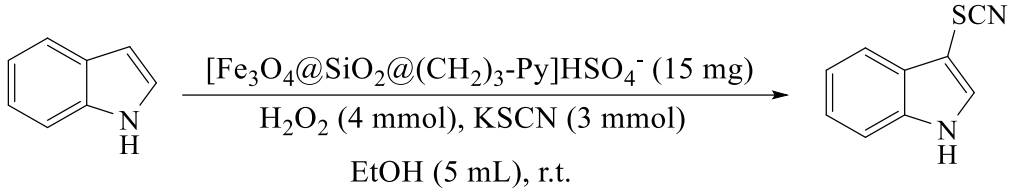
Entry	H_2O_2	Load of catalyst	Time (min)	Yield (%)[a]
1	H_2O_2 (2 mmol)	15 mg	10	95
2	H_2O_2 (4 mmol)	15 mg	10	97
3	H_2O_2 (6 mmol)	15 mg	15	92
4	H_2O_2 (8 mmol)	15 mg	15	90

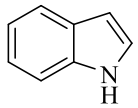
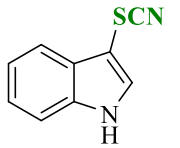
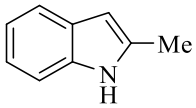
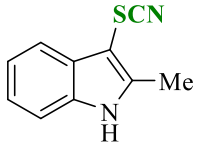
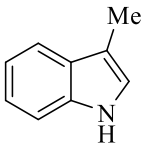
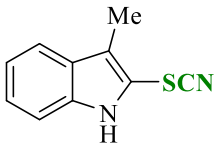
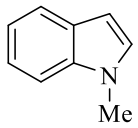
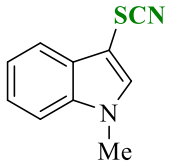
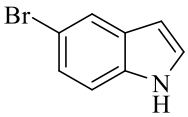
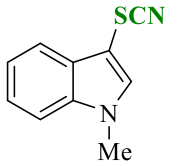
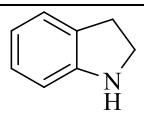
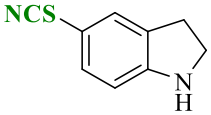
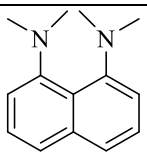
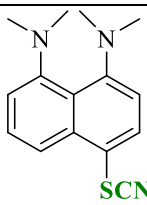
[a] Isolated yield

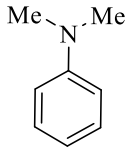
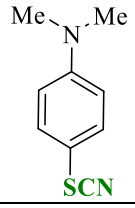
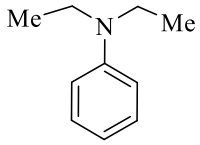
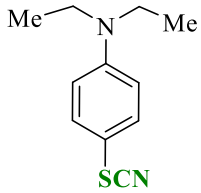
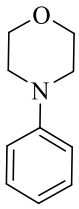
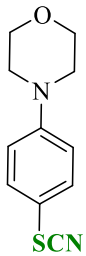
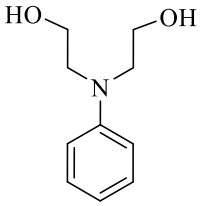
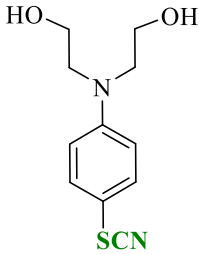
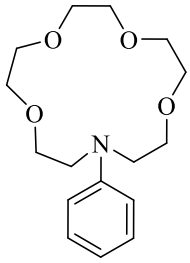
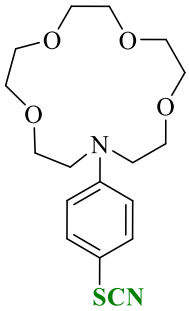
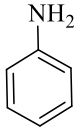
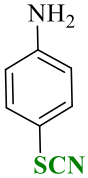
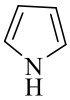
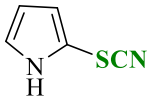
After optimizing the reaction conditions, the outcome data implied that the 1*H*-indole (1 mmol) at the presence of 15 mg of $[Fe_3O_4@SiO_2@(CH_2)_3\text{-}Py]HSO_4$ as a reusable magnetic nanocatalysts, KSCN (3 mmol), H_2O_2 (4 mmol) in EtOH (5 mL) as solvent at room temperature is the optimal reaction condition. So, we used several indoles (indole with electron-releasing substituents, anilines, and pyrrole) to furnish the corresponding products (Table 4). As can be seen in Table 4, the reactions for all the

substrates including the pyrrole, anilines, and indoles were found to proceed smoothly toward the aryl and heteroaryl thiocyanates derivatives **3a-b** in excellent yields with the short reaction time.

Table 4. Synthesis of aryl and heteroaryl thiocyanates derivatives in the presence of $[Fe_3O_4@SiO_2@(CH_2)_3\text{-}Py]HSO_4$



Entry	Substrate	Product		Time (min)	Yield (%)[a]
1			**2a**	10	97
2			**2b**	8	95
3			**2c**	24 h	-
4			**2d**	8	90
5			**2e**	40	91
6			**2f**	60	87
7			**2g**	35	86

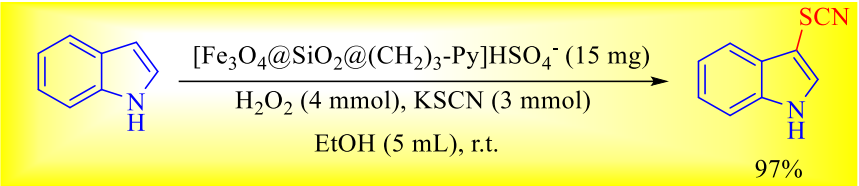
8			**2h**	35	88
9			**2i**	30	88
10			**2j**	45	87
11			**2k**	35	85
12			**2l**	35	85
13			**2m**	10	93
14			**2n**	30	88

[a] Isolated yield

It is worthwhile that the acidic ionic liquid based silica-coated Fe_3O_4 nanoparticles can be recyclable for 4 times. For this purpose, we selected the reaction 1*H*-indole (1 mmol) at the presence of 15 mg of

$[Fe_3O_4@SiO_2@(CH_2)_3\text{-}Py]HSO_4$, KSCN (3 mmol), H_2O_2 (4 mmol) in EtOH (5 mL) as a model reaction for the synthesis of 3-thiocyanato-1*H*-indole **2a**. After 20 min (the end of the cycle) the acidic ionic liquid based silica-coated Fe_3O_4 nanoparticles were separated by external magnet, washed, and dried for next run. The obtained data from the reusability of catalyst are presented in Table 5.

Table 5. The recyclability of the catalyst for the synthesis of 3-thiocyanato-1*H*-indole in during 30 min



	Run	1	2	3	4
	Yield (%)	97	96	95	92

Furthermore, inorder to show the efficacy of the our method compared with other methods that previously reported, we have compared our results obtained in this work for the synthesis of aryl and heteroaryl thiocyanates derivatives **2a-n** at the presence of acidic ionic liquid based silica coated Fe_3O_4 nanoparticles $[Fe_3O_4@SiO_2@(CH_2)_3\text{-}Py]HSO_4$ as a reusable magnetic nanocatalysts with other results reported in the literature (Table 6). As seen in Table 6, this protocol avoids from some drawbacks such as high temperatures, long reaction times, excessive reagents, toxic oxidant, low yields, and toxic reagent and solvent. It was found that, our method wasmore beneficial from the viewpoints of accessibility and economy.

Table 6. Comparison of the efficiency of $[Fe_3O_4@SiO_2@(CH_2)_3\text{-}Py]HSO_4$ with other methods for the synthesis of aryl and heteroaryl thiocyanates derivatives **2a-n**

Entry	Catalyst	Reaction conditions	Time (min)	Yield (%)	Ref.
1	Iodine	NH_4SCN, CH_3OH, r.t.	20-50	82-96	15
2	Diethyl azodicarboxylate	NH_4SCN, CH_3CN, r.t.	6-150	75-91	21
3	$SiO_2@\{[Pyridine\text{-}SO_3H]SCN\}$	EtOH:H_2O, r.t	20-70	84-95	27
4	SBSA	H_2O, KSCN, r.t.	10-270	71-92	28
5	SSA	UHP, H_2O, KSCN, r.t.	7-75	71-95	28
6	Visible-Light	NH_4SCN, air		-	30
7	{[PSA]Cl}	EtOH:H_2O, r.t	2-10 h	82-93	31
8	Graphite electrode	NH_4SCN, CH_3OH	25-90	10-96	38
9	$[Fe_3O_4@SiO_2@(CH_2)_3\text{-}Py]HSO_4$	EtOH, r.t	8-45	85-97	-

Conclusion

In this work, we have developed an efficient and simple one-pot reaction includingacidic ionic liquid based silica-coated Fe_3O_4 nanoparticles [Fe_3O_4@SiO_2@$(CH_2)_3$-Py]HSO_4 as an efficient and reusable magnetic nanocatalysts with various aromatic and heteroaromatic compounds (pyrrole, anilines, and indoles) to access aryl and heteroaryl thiocyanates derivatives **2a-n** in moderate to excellent yields (up to 97% isolated yield) and short reaction time. The reaction useda green, readily available, inexpensive, and simple oxidant and solvent. This protocol was found to be simple, high-yielding, cost-effective, and eco-friendly.

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Conflict of Interest

We have no conflicts of interest to disclose.

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